Name of Organization: USDA, ARS-Beltsville

Type of Organization: Federal Agency

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Project Title: Exposure and Effects of Sediment Reserves of APEs

Project Category: Emerging Issues

Rank by Organization (if applicable): 0

Total Funding Requested ($): 287,000 **Project Duration:** 2 Years

Abstract:

Evidence is now emerging that suggest that alkylphenols and alkylphenol ethoxylates will build up in sediments at sites where heavy discharges have occurred. This Project will address the issue of the sequestration and release of alkylphenols and alkylphenol ethoxylates from sediment deposits in a riverine environment. Sequestration will be determined by examining depositional areas downstream of a major outfall, e.g. areas in Rouge or Detroit rivers. The depositional history will be mapped using analysis of APEs in representative sediment grabs and 1-3 sedment cores, with dating of the core segments. All of the sediment APE measures will include measurement of ethoxy substitution up to 20. Since the toxic forms are produced through degradation of the longer chain ethoxylates that accumulate in sediments, availability of the shorter chain homologes will be addressed by sampling fish inhabiting the waters above the sites and water sampling and analysis under different flow regimes. The possible impact of these contaminants will be addressed by utilizing a screening system using Microtox and health examinations on the fish. Frequent analyses utilizing the Microtox will be employed on water sampled above the sediment depositional region and downstream to assess the possible immediate impact of discharges from the sediment and to determine how far these effects extend downstream and under different flow regimes. These chemicals are present in many municipal and industrial discharges and, therefore the results of this study will have implications to all Great Lakes Areas of Concern.

Geographic Areas Affected by the Project

States:

- ☐ Illinois
- ☐ Indiana
- ☒ Michigan
- ☐ Minnesota
- ☐ New York
- ☐ Pennsylvania
- ☐ Wisconsin
- ☐ Ohio

Lakes:

- ☐ Superior
- ☐ Huron
- ☐ Michigan
- ☒ Erie
- ☐ Ontario
- ☐ All Lakes

Geographic Initiatives:

☐ Greater Chicago ☐ NE Ohio ☐ NW Indiana ☒ SE Michigan ☐ Lake St. Clair

Primary Affected Area of Concern: Detroit River, MI

Other Affected Areas of Concern: Results will have implications to all areas of concern that are contaminated with these chemicals.

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

Evidence is now emerging that suggest that alkylphenols and alkylphenol ethoxylates (APEs) will build up in sediments at sites where heavy discharges have occurred. Once in the sediment it appears highly likely that slow release to the water column will occur. Also the surficial sediments in these regions will offer ready exposure to biota inhabiting these sites. The likeliest sources of the sediment deposition regions discussed above would be sewage outfall locations, and such evidence has been document, especially for sewage treatment plants that functioned poorly in the past or those that only provided primary treatment (Shang et al. 1999, Ferguson et al. 1999). Alkylphenols and alkylphenol ethoxylates are a universal contaminant in the environment, especially aquatic systems. Their appearance at sewage treatment plant outfalls is well documented (Ahel and Giger1985, Barber et al. 1999). This occurrence in aqueous discharges has led to concern about their potential impact on indigenous fish and evidence exists that they can cause reproductive effects on fish downriver of sewage treatment outfalls (Jobling et al. 1998), possibly leading to exposure of bottom-feeding organisms at these sites. There is evidence that these chemicals persist in sediments long after discharges are eliminated. Degradation half-lives of 60 years were estimated for deposits in a site off the coast of Vancouver, BC (Shang et al. 1999). Little is known about the processes which impact these deposits or their occurrence and extent at known sites of past and present discharges. Kannan et al. (1999) reported extensive contamination of sediment with the non-ethoxylated octyl and nonyl APEs in surficial sediment of the Detroit River, 17 ppm in Conners Creek area and 60 ppm near the Shell outfal on the Rouge River. Had the ethoxylated forms been measured, total APE concentrations should easily double or triple (Shang et al. 1999). We propose to seek out one or more of these sites, conduct studies to screen for their impact, using Microtox; determine the depth and aerial extent of the non-ethoxylated and ethoxy-substituted family of APEs using sediment sampling and analysis. We also plan to access their cycling at the sediment water interface, especially as they degrade to their less ethoxylated or carboxylated forms and finally to access the availability of the more toxic (zero to 5 ethoxy-substituted) APE forms to biota and fish at these sites.

References:

Shang, D.Y., Ikonomoou, M.G., Macdonald, R.W. 1999. Quantitative Determintion of nonylphenol polyethoxylate surfactants in marine sediment using normal-phase liquid chromatography-electrospray mass spectometry. J. of Chromatography A, 849: (2) 467-482.

Ferguson, P.L., Brownalee, B.J., Iden, C.R. 1999. Distribution and fate of alkylphenol ethoxylate metabolites in the New York Harbor complex. Abstract, 20th Annual Meeting, Society of Toxicology and Chemistry, pg. 52.

Kannan, K., Yamashita, N., Kober, J., Ostaszewski, A., Summer, C.; Giesy, J.P. 1999. Distribution of trace organic contaminants in sediment of the Detroit and Rouge Rivers. Abstract, 20th Annual Meeting, Society of Toxicology and

Chemistry, pg. 224.

Barber, L.B., Brown, G.K., Zaugg, S.D. 2000. Potential endocrine disrupting organic chemicals in treated municipal wastewater and river water. eds, Keith, L.H., Jones-Lepp, T.L., Needham, L.L. Analysis of Environmental Endocrine Disrutpors. ACS Symposium Series 747, American Chemical Society, Washington D.C. p 97-123.

Jobling, S., Nolan, M., Tyler, C.R., Brighty, G., Sumpter, J.P. 1998. Widespread sexual disruption in wild fish. Environ. Toxicol. Chem. 15(2): 194-202.

Ahel, M. Giger, W. 1985. Determination of alkylphenols and alkylphenol mono- and diethoxylates in environmental samples by high-performance liquid chromatography. Anal. Chem. 57:1577-1583.

Proposed Work Outcome:

We propose to identify a sediment depositional site where historical buildup of APEs exist. Such sites likely occur downstream of Connors Creek or in the Rouge River, a tributary to the Detroit River. Once identified we plan to carry out extensive sediment analyses to 1) characterize the depth profile for APE deposition, 2) determine the aerial extent of the zones of highest levels and 3) apply an effects screening tool, such as Microtox, and 4) Examine availability to biota by sampling fish both within and outside the contaminated sediment zone. Availability will be assessed through the toxicity screening assay available with the Microtox system. Concurrently, analytical studies of APE distribution in sediment profiles in the selected areas of concern will be conducted so that recent historical deposition and cycling can be evaluated. Selected sediment core dating (1-3 samples) will be provided utilizing isotope methods. Indigenous fish species will be sampled both within and outside the area of contaminations to determine differences in uptake. Since there may be seasonal and delayed impacts on these fish, samplings and concomittant biological impact assessments will be determined at bi- monthly intervals over a 1 year time span. Brown Bullheads or other typical resident bottomfeeding fish will be sampled along with a representative top predator fish such as largemouth bass. The primary assay to be preformed will be alphenols (octyl and nonyl) and the alkylphenol ethoxylates (Octyl and Nonyl 1 to 5 EO). For sediment, the ethoxylate groups will be determined up to 20 substitutions, so that the entire pattern can be followed. Doing this complete set of ethoxylated forms of the APEs better accounts for the materials as they are discharged and can be accomplished by recently improved LC/MS methods(Shang et al. 1999, Ferguson et al. 1999). Water collections and analyses will be performed to assess loss through slow leaching. Included in these analyses will also be the carboxylate metabolites which are indicatative of oxidative degradation. Biological endpoints that will be monitored in the fish will be full health exams including gonad histology, sperm and egg viability, and collection of blood to measure for vitellogenin, estradiol and testosterone. The remaining tissue will be retained for measurement of lower ethoxy substituted alkylphenols and ethoxylates (0 to 5 ethoxy substitutions.)

Field sites are conveniently located near to the Great Lakes Science Center, Ann Arbor Michigan. This will be a collaborative project with staff at this laboratory, primarily Dr. Dora Passino-Reader and James Hickey for collection, Microtox screening and sample preparations and archiving. For the fish samples the laboratory staff will further assist in their preparation for extraction and storage prior to final analysis. Quantitative APE analyses will be conducted at the USDA laboratory utilizing LC/MS, LC/fluorescence and GC/MS, depending on which produces the most sensitive and reliable results. Stephen Smith, staff biologist for USGS/ BRD in Reston, will conduct the biological endpoint and biological health workups for fish, including contracting for vitellogenin, testosterone, estrogen and histopathology. Assistance will be obtained from the Michigan DEQ, Art Ostaszewski, for collection of the sediment samples. Results will have implications in all freshwater systems where large deposits of these chemicals occur, including the Great Lakes Areas of Concern.

Project Milestones:	Dates:
Project Start, procure equip.	09/2000
Site identification (Microtox Screen)	09/2000
Sediment sampling	10/2000
Water (Microtox/ape data)	11/2001
Fish sampling completed	11/2001
Biological and Residues done	08/2002
Final report	09/2002
Project End	10/2002

☐ Project Addresses Environmental Justice

If So, Description of How:

N/A

☒ Project Addresses Education/Outreach

If So, Description of How:

Results of this study will be communicated to the detroit River RAP committes and Lake Erie LAMP teams. Results will also be presented to appropriate fora under the auspices of the International Joint Commission and the Great Lakes Fisheries Commission. Presentations will be made at professional society meetings including IAGLR and SETAC.

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	110,000	60,000
Fringe:	35,000	20,000
Travel:	7,000	5,000
Equipment:	25,000	17,000
Supplies:	60,000	10,000
Contracts:	20,000	0
Construction:	0	0
Other:	0	0
Total Direct Costs:	257,000	112,000
Indirect Costs:	30,000	0
Total:	287,000	112,000
Projected Income:	0	0

Funding by Other Organizations (Names, Amounts, Description of Commitments):

In-kind funding provided by the USDA-Agricultural Research Service and the USGS-Great Lakes Science Center and USGS/ NAWQA through utilization of facilities and staff involved with the project.

Description of Collaboration/Community Based Support:

Dora Passino-Reader/ James Hickey
USGS, Great Lakes Research Center, Ann Arbor,MI

Stephen Smith
NAWQA, BRD, USGS, Reston, VA

Steve Rheume
USGS, WRD, Lansing MI

Arthur Ostaszewski
Michigan Dept. of Environmental Quality on identifying sites and possible assistance at collection.

John Hartig, River Navigator, Detroit River Heritage Program

Laura Lodisio, EPA S.E. Michigan Initiative